Diode Laser Modification of Ceramic Material Surface Properties for Improved Wettability and Adhesion

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Abstract

To date, very little work has been published with regard specifically to the use of lasers for modifying the surface properties of materials in order to improve their wettability and adhesion characteristics. Using a 60 W high power diode laser (HPDL) the effects of HPDL radiation on the wettability and adhesion characteristics of certain ceramic materials have been determined. It was found that laser treatment of the materials surfaces' modified the surface energy and accordingly, wetting experiments, by the sessile drop technique using a variety of test liquids, revealed that laser treatment of the range of ceramic materials surfaces resulted in a decrease in the contact angles. The work shows clearly that laser radiation can be used to alter the wetting and adhesion characteristics of a number of ceramic materials by means of changing the surface energy.

Keywords: high power diode laser, ceramic, contact angle, surface energy, wettability

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1. Introduction

The understanding of the influence solid-substrate surface energy has on the wettability characteristics is of great importance. Both scientists and engineers alike have a distinct interest in the mechanisms of the phenomena since it is one of the principal influences on the wetting, and subsequent adhesion, of coatings, etc., on a selected substrate; therefore, ultimately influencing the in-service performance of any such article. This paper details work that has been conducted using a 60 W high power diode laser (HPDL) in order to determine the effects of HPDL radiation on the surface energy, and consequently the wettability characteristics, of a variety of engineering ceramic materials.

Although little work has been carried out to investigate employing lasers to modify the surface properties of materials in order to improve their wettability characteristics, it is nevertheless recognised within the currently published work that laser irradiation of material surfaces can affect changes in the materials wettability characteristics. However, the reasons for these changes with regard to changes in the materials surface energy are not reported. Zhou et al [1, 2] have carried out work on laser coating of aluminium alloys with ceramic materials (SiO_2, Al_2O_3, etc.), reporting on the well documented fact that generated oxide layers often promote metal/oxide wetting. Bahners et al [3, 4], have observed and accounted comprehensively for the changes in technical properties of various textile fibres, including adhesion and wetting properties, with a view to developing an alternative to the conventional methods of chemical agents addition or wet-chemical pre-processing. Similarly, Kappel [5] has shown that the texturing of ceramics with an excimer laser can improve the adhesion strength by up to 20%. Such an improvement is said to be due to the formation of raised microscopic protrusions over the surface.

2. Theoretical background

When a drop of liquid is in contact with a solid surface, the final shape taken by the drop, and thus whether it will wet the surface or not, depends upon the relative magnitudes of the molecular forces that exist within the liquid (cohesive) and between the liquid and the solid (adhesive) [6]. The index of this effect is the contact angle, θ, which the liquid subtends with the solid. The adhesion intensity of a liquid to a solid surface is known as the work of adhesion, W_{ad}, and is related to the liquid surface energy, γ_{lv}, by the Young-Dupre equation:

$$W_{ad} = \gamma_{lv}(1+\cos\theta) \tag{1}$$

The influence of the substrate surface roughness on the wetting contact angle is also of great importance, being described by Wenzel's equation:

$$r(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv}\cos\theta_w \tag{2}$$

where, r is the roughness factor defined as the ratio of the real and apparent surface areas, γ_{sv} is the solid surface energy, γ_{sl} is the solid-liquid surface energy and θ_w is the contact angle for the wetting of a rough surface. Clearly, as Equation (2) shows, the influence of surface roughness on the contact angle is to affect an increase in the contact angle. Thus, the smoother the contact surface is, the smaller the contact angle will be.

The intermolecular attraction which is responsible for surface energy, γ, results from a variety of intermolecular forces whose contribution to the total surface energy is additive [7]. The majority of these forces are functions of the particular chemical nature of a certain material, and as such the total surface energy (γ) comprises of γ^p (polar or non-dispersive interaction) and γ^d (dispersive component). As such, W_{ad} can be expressed as the sum of the different intermolecular forces that act at the interface [7]:

$$W_{ad} = W_{ad}^d + W_{ad}^p = 2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2} \tag{3}$$

By equating Equation (3) with Equation (1), the contact angle for solid-liquid systems can be related to the surface energies of the respective liquid and solid by

$$\cos\theta = \frac{2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2}}{\gamma_{lv}} - 1 \tag{4}$$

3. Experimental procedures

The laser used in the study was a 60 W HPDL, emitting at 810nm ±20nm. The laser beam was delivered to the samples by means of a 600μm core diameter optical fibre, the end of which was connected to a 2:1 focusing lens assembly mounted on the z-axis of a 3-axis CNC table. The defocused laser beam was fired across the surfaces of the ceramic materials by traversing the samples beneath the laser beam using the x- and y-axis of the CNC table at speeds of 5-8 mm/s, whilst 3 l/min of coaxially blown O_2 assist gas was used to shield the laser optics.

The liquids used for the wetting experiments were human blood, human blood plasma, glycerol and 4-octanol. The test liquids, along with their total surface energy (γ_2) as well as the dispersive (γ_2^d) and polar (γ_2^p) components, are detailed in Table 1. The solid materials used as substrates in the wetting experiments were squares (10 x 10mm with a thickness of 3mm) of common engineering ceramic materials; unglazed ceramic tile, clay quarry tile, Al_2O_3 and SiO_2-TiO_2 (crystalline). The contact surfaces of the materials were polished (3μm) and cleaned in an ultrasonic bath.

The wetting experiments were carried out in atmospheric conditions at a temperature of 20^0C. The droplets were released in a controlled manner onto the surface of the test substrate materials (treated and untreated) from the tip of a micropipette, with the resultant volume of the drops being approximately 6×10^{-3} cm^3. Each experiment lasted for three minutes with profile photographs of the sessile drops being obtained every minute, with the contact angle subsequently being measured. The experimental results showed that throughout the period of the tests no discernible change in the magnitude of the contact angle occurred.

4. Results and discussion

As one can see from Table 2, laser irradiation of the substrate material surfaces resulted in all the materials displaying a reduction in the contact angle. One explanation for this is that the surfaces obtained after laser treatment are significantly smoother than the original untreated surfaces (Fig.1 and Fig.2). Thus, according to Equation (2), the smoother surface will inherently result in a reduction in the contact angle.

Also, the improvements in the wetting action experienced by all the materials will have certainly been influenced by the increase in the surface oxygen content of the ceramic materials as a result of the laser treatment; since this is known to increase the likelihood of wetting [8, 9]. Indeed, by mounting cross-sectioned samples of the untreated and laser treated ceramic materials next to each other, and examining them both simultaneously by means of energy dispersive x-ray analysis (EDX), it was possible to

determine the relative element content of oxygen near the material surfaces. As one can see from Fig. 3, the surface oxygen content was observed to increase in all the ceramic materials after laser treatment due to the oxidisation on the laser treated surfaces of the materials, thus indicating that oxygen enrichment of the laser treated ceramic material surfaces was active in promoting wetting and adhesion [8, 9].

It is possible to estimate the dispersive component of the ceramic materials surface energy γ_{sv}^{d} by using Equation (4), and plotting the graph of cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$ (Fig. 3). Thus the value of γ_{sv}^{d} is estimated by the gradient $(=2(\gamma_{sv}^{d})^{1/2})$ of the line which connects the origin (cos θ = -1) with the intercept point of the straight line (cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$) correlating the data point with the abscissa at cos θ = 1 [7]. The values of γ_{sv}^{d} for the untreated and laser treated ceramic materials are shown in Table 3. From the best-fit plots of cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$, it was found that the ordinate intercept points of the untreated ceramic materials-liquid systems were closer to cos θ = -1 than those for the laser treated ceramic materials-liquid systems. This indicates that, in principle, dispersion forces act mainly at the ceramic materials-liquid interfaces resulting in poor adhesion [7, 10]. In contrast, the best-fit straight line for the laser treated ceramic materials-liquid systems intercepted the ordinate considerably higher above the origin. This is indicative of the action of polar forces across the interface, in addition to dispersion forces, hence improved wettability and adhesion is promoted [7, 10].

It is not possible to determine the value of the polar component of the ceramic materials surface energy γ_{sv}^{p} directly from plots of cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$. This is because the intercept of the straight line (cos θ against $(\gamma_{lv}^{d})^{1/2}/\gamma_{lv}$) is at $2\left(\gamma_{sv}^{p}\gamma_{lv}^{p}\right)^{1/2}/\gamma_{lv}$, and thus only refers to individual control liquids and not the control liquid system. However, it has been established that the entire amount of the surface energies due to dispersion forces either of the solids or the liquids are active in the wettability performance [7, 11]. Thus it is possible to calculate the dispersive component of the work of adhesion, W_{ad}^{d} from Equation (3). The results revealed that for each particular control liquid in contact with both the untreated and laser treated ceramic materials surfaces, W_{ad} could be correlated with W_{ad}^{d} by a linear relationship. Also, for the control test liquids used, a linear relationship between the dispersive and polar components of the control test liquids surface energies could also be deduced. By combining these linear relationships and differentiating with respect to $\left(\gamma_{lv}^{d}\right)^{1/2}$, the following can be derived:

$$\left(\gamma_{sv}^{p}\right)^{1/2} = \frac{\left(\gamma_{sv}^{d}\right)^{1/2}\left(a-1\right)}{1.3} \qquad (5)$$

From a plot of the linear relationship between W_{ad}^{p} and W_{ad}^{d}, a was determined for the untreated and laser treated ceramic materials. Since γ_{sv}^{d} has already been determined for the untreated and laser treated ceramic materials from the plots of Equation 4, it is possible to calculate γ_{sv}^{p} for untreated and laser treated ceramic materials using Equation (5) (see Table 3)

As Table 3 shows clearly, HPDL treatment of the surface of the ceramic materials has led to an increase in the polar component of the surface energy γ_{sv}^{p}, thus improving the action of wetting and adhesion. Such changes in the surface energy of the ceramic materials after laser treatment are due to the fact that HPDL treatment of the surface of these ceramic materials results in partial vitrification of the surface; a transition that is known to affect an increase in γ_{sv}^{p} [12].

5. Conclusion

Laser treatment of the surfaces of all the selected ceramic materials resulted in a reduction in the contact angles with the test liquids. Improvements in the wetting action of the ceramic materials after laser treatment were identified as being due to:

- The laser sintering of the ceramic materials surfaces reducing the surface roughness, thus directly reducing the contact angle θ.
- The increase in the polar component of the surface energy, γ_{sv}^{p}, after laser treatment as a result of the partial laser vitrification of the glass forming elements within the ceramic materials composition, thus improving the action of wetting and adhesion.
- The increase in the surface oxygen content of the ceramic materials resulting from laser treatment was identified as further promoting the action of wetting.

This work demonstrates that it is possible to alter the wetting characteristics of the selected ceramic materials using the HPDL. Moreover, the findings of this work show that with the use of laser radiation it is a distinct possibility that the wetting characteristics of many other materials could be altered, based on similar mechanisms identified for the selected ceramic materials.

Acknowledgements

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Fig. 1

(a) (b)

Fig.2

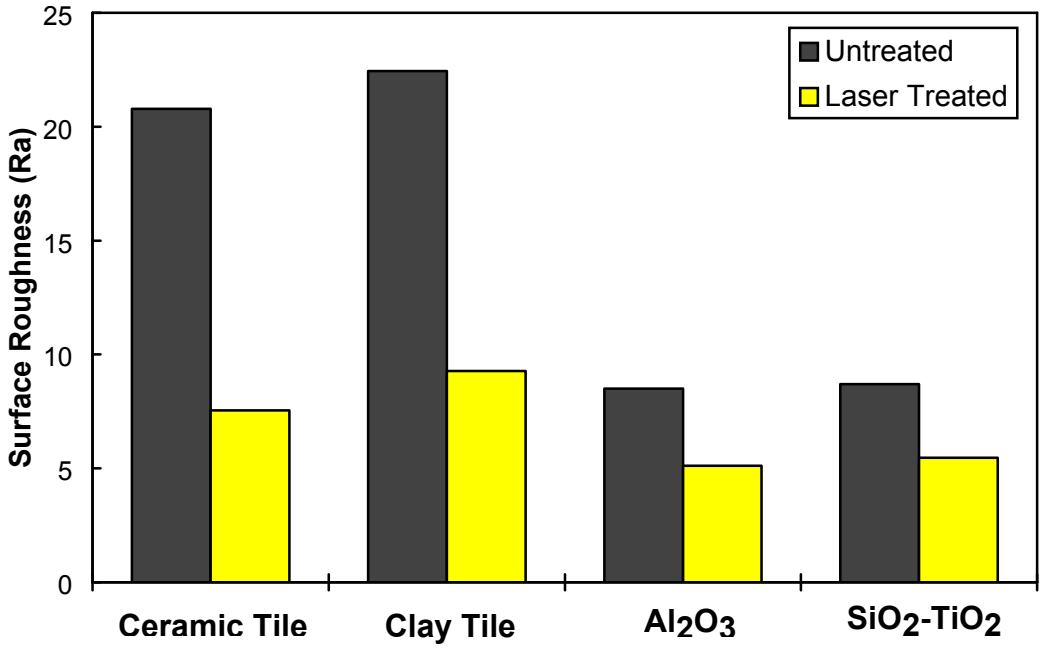

Fig. 3

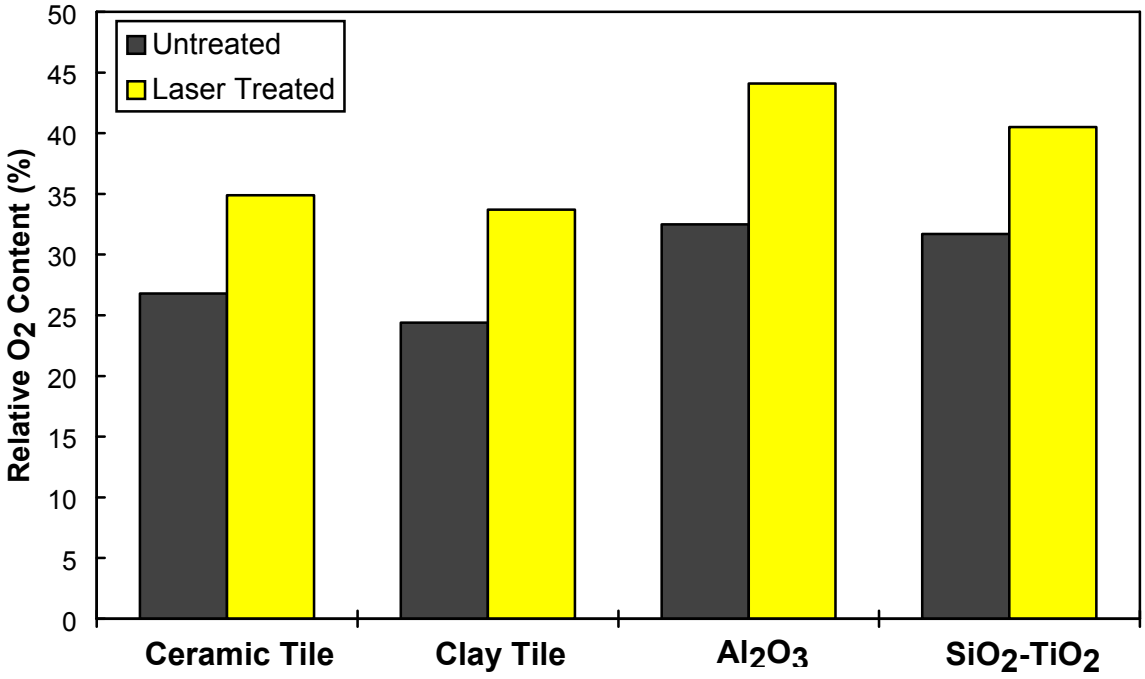

Fig. 4

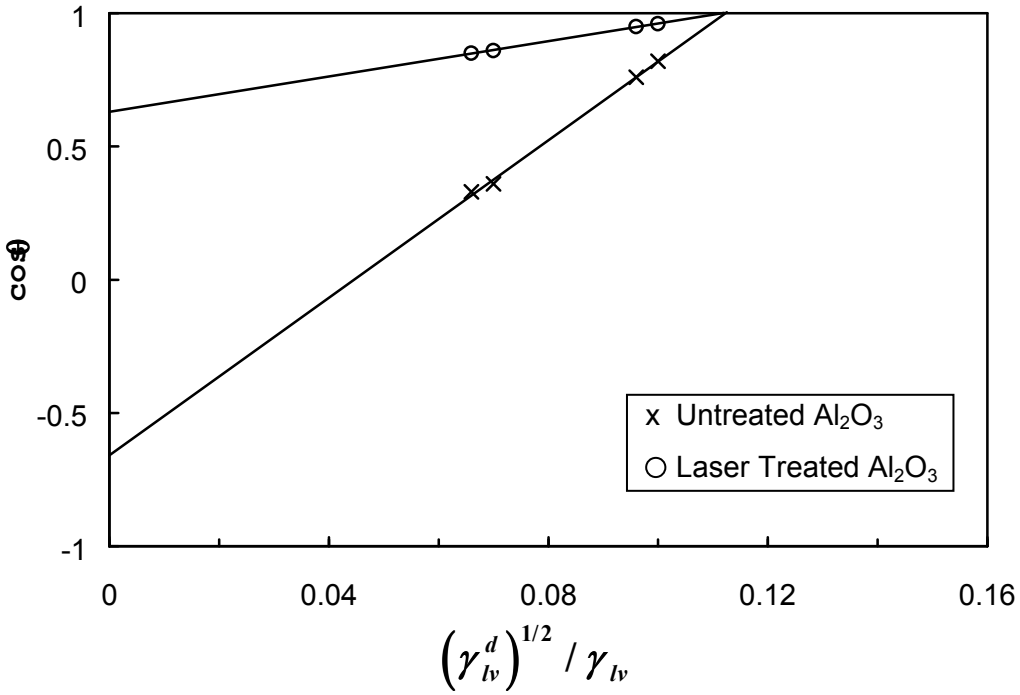

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Table 1 : Total surface energy (γ_{lv}) and the dispersive (γ_{lv}^{d}) and polar (γ_{lv}^{p}) components for the selected test liquids [6].

Table 2 : Measured contact angle values for the ceramic materials before and after HPDL irradiation. (UT = untreated LT = Laser Treated)

Table 3 : Measured surface energy values for the ceramic materials before and after HPDL irradiation. (UT = untreated LT = Laser Treated)

Table 1

Liquid	γ (10^{-3}J/m^2)	γ_{lv}^{d} (10^{-3}J/m^2)	γ_{lv}^{p} (10^{-3}J/m^2)
Human Blood	47.5	11.2	36.3
Human Blood Plasma	50.5	11.0	39.5
Glycerol	63.4	37.0	26.4
4-Octanol	27.5	7.4	20.1

Table 2

Substrate	**Contact Angle (θ)**							
	Blood		**Plasma**		**Glycerol**		**4-octanol**	
	UT	**LT**	**UT**	**LT**	**UT**	**LT**	**UT**	**LT**
Ceramic Tile	69.00	30.68	70.73	31.79	40.54	18.19	34.92	16.26
Clay Tile	73.14	47.16	76.11	49.46	57.32	32.86	53.84	29.54
Al_2O_3	76.11	61.32	78.46	62.61	55.25	50.95	50.94	48.70
SiO_2-TiO_2 (cryst)	56.63	38.74	60.66	40.54	35.90	28.36	30.68	25.84

Table 3

Surface Energy	**Substrate Material**							
	Ceramic		**Clay Tile**		**Al_2O_3**		**SiO_2-TiO_2**	
	UT	**LT**	**UT**	**LT**	**UT**	**LT**	**UT**	**LT**
Dispersive, (γ_{sv}^{d}) (10^{-3}J/m^2)	79.72	76.95	66.10	68.30	59.17	62.00	76.95	64.00
Polar, (γ_{sv}^{p}) (10^{-3}J/m^2)	4.25	29.14	0.39	10.10	0.00	2.67	3.08	15.51